Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

Table S1:

AgNPs-1					
Shell	N^{bulk}	R[Å]	σ^2 [$\times 10^2$Å^2]		
Ag-Ag_I	12	2.846(8)	1.1(3)	R_o^2	0.05
Ag-Ag_{II}	6	4.02	1.9(7)		
Ag-Ag_{III}	24	4.93	2.5(9)	x	0.77(5)
Ag-$Ag_{IV}^{(1)}$	12	5.69	4.9(12)	p	6.2(1.5)
Ag-$Ag_{IV}^{(2)}$	24	8.05	3.7		
Ag-$Ag_{IV}^{(3)}$	12	9.86	2.3(9)		
Ag-S	2	2.42(2)	1.3(6)		
Ag-Ag	5	3.30(9)	2.7(9)		
AgNPs-2					
Shell	N^{bulk}	R[Å]	σ^2[$\times 10^2$Å^2]		
Ag-Ag_I	12	2.858(9)	0.9(3)	R_o^2	0.03
Ag-Ag_{II}	6	4.04	1.1(3)		
Ag-Ag_{III}	24	4.95	2.0(9)	x	0.72(5)
Ag-$Ag_{IV}^{(1)}$	12	5.72	7.2(25)	p	3.5(8)
Ag-$Ag_{IV}^{(2)}$	24	8.08	4.5		
Ag-$Ag_{IV}^{(3)}$	12	9.90	2.0(7)		
Ag-S	2	2.38(3)	1.3(4)		
Ag-Ag	5	3.19(6)	1.7(2)		
Ag-Ag	5	3.62(8)	1.7		

Table S1: Results of Ag K edge data analysis. The Ag-$Ag_{IV}^{(i)}$ are respectively the single Ag_o-Ag_{IV}-Ag_o,(Ag_o being the absorber) and multiple scattering: Ag_o-Ag_I-Ag_{IV}-Ag_o and Ag_o-Ag_I-Ag_{IV}-Ag_I-Ag_o contributions to the fourth Ag fcc shell. A strong correlation is found among the σ^2 of the three contributions, we found that constraining the σ^2 of Ag-$Ag_{IV}^{(2)}$ to the average value between σ^2 of Ag-$Ag_{IV}^{(1)}$ and Ag-$Ag_{IV}^{(3)}$ reduces such a correlation making the refinements more stable and reproducible.

The analysis of AgNPs-2 requires two Ag-Ag next neighbour shell around 3.2 and 3.6 Å this signaling relatively thicker and more ordered Ag_2S-like shell around the metallic Ag fcc core. In the fitting the disorder factors were kept the same as the AgNPs-1 sample to avoid correlation effects.

The error bars on the parameters have been estimated looking at the variance of the best fit parameters obtained by several refinement attempts. In case of σ^2 the reported errors are about 50-80%larger than those given by statistical analysis of a single refinement but give more realistic uncertainty. A relatively strong correlation is found among the disorder factors σ^2 and the value of p (reflecting on the average size of the NPs) giving the uncertainty on p as high as 25-30%.

The R_o^2 is reported to quantify the best fit quality.

Table S2.

S K edge					
AgNPs-1					
Shell	N^{bulk}	R[Å]	σ^2 [$\times 10^2$Å^2]		
S-Ag	4	2.46(3)	1.5	R_o^2	0.11
S-Pt	1	2.31(2)	1.3(3)		
S-P	2	3.20(2)	1.0(4)	y	0.61(5)
S-C$^{(1)}$	1	4.25(3)	1.7(5)		
S-C$^{(2)}$	2	4.25	1.9		
S-C$^{(3)}$	1	4.25	2.1(7)		
AgNPs-2					
Shell	N^{bulk}	R[Å]	σ^2[$\times 10^2$Å^2]		
S-Ag	4	2.48(2)	1.5	R_o^2	0.09
S-Pt	1	2.33(2)	0.9(3)		
S-P	2	3.20(2)	1.3(4)	y	0.51(5)
S-C$^{(1)}$	1	4.38(5)	1.(5)		
S-C$^{(2)}$	2	4.38	1.3		
S-C$^{(2)}$	1	4.38	1.5(5)		

Table S2: Results of S K edge data analysis. The S K edge EXAFS spectra have been fitted assuming S in the Ag_2S-like phase (shell) and bonded to tiol tails (mainly the S atoms at the N surface). The k-range of the S spectra is relatively short and the presence of Pt additional edge disturbs the analysis. Therefore the quality of the results at the S K edge is worse than those obtained at the Ag. Moreover we imposed some constraint to avoid strong correlation among the parameters. In particular after preliminary attempts the σ^2 of S-Ag shell were fixed to 1.5×10^2Å^2 in both the samples. The S-C$^{(i)}$ represent the single and multiple scattering contributions due to the collinear S-Pt-C configuration (namely S-C-S, S-Pt-C-S, S-Pt-C-Pt-S scattering paths). We assumed the S-Pt-C angle equal to 180° and we constrained the σ^2 of S-C$^{(2)}$ as the mean value between S-C$^{(1)}$ and S-C$^{(3)}$. As for the Ag K edge analysis the error bars on the parameters have been estimated looking at the variance of the best fit parameters obtained by several refinement. The R_o^2 is reported as a reference of the best fit quality.

Table S3.

sample	signal	BE (eV)	FWHM (eV)	* I ratios	Assignment
Ag/complex 1 = 0.7/1 (AgNPs-1)					
	C1s	285.11 286.76 288.60	1.65 1.65 1.65	89.93% 8.96% 1.11%	C-C C-S C=O
	$S2p_{3/2}$	160.75 163.05	1.65 1.65		S-Ag S-H or S-S
	$Pt4f_{7/2}$	72.00 73.00	2.17		PtDEBP-like
	$P2p_{3/2}$	130.31	1.75	1	PtDEBP-like
	$Ag3d_{3/2}$	368.24 368.96	0.95 0.95	78.36% 21.64%	Ag(0) Ag (δ^+)
Ag/complex 1 = 1/1 (AgNPs-2)					
	C1s	285.11 286.76 288.60	1.65 1.65 1.65	89.93% 8.96% 1.11%	C-C C-S C=O
	$S2p_{3/2}$	160.75 163.05	1.65 1.65		S-Ag S-H or S-S
	$Pt4f_{7/2}$	72.00 73.00	2.17		PtDEBP-like
	$P2p_{3/2}$	130.31	1.75	1	PtDEBP-like
	$Ag3d_{3/2}$	368.24 368.96	0.95 0.95	78.36% 21.64%	Ag(0) Ag (δ^+)

Table S3: SR-XPS data collected on samples AgNPs-1 and AgNPs-2.

Figure S1.

Ag-Link-H

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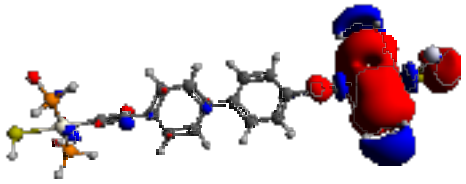
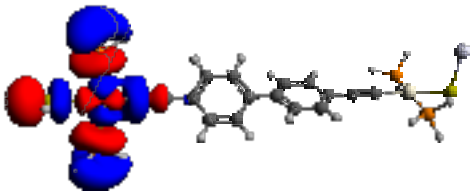
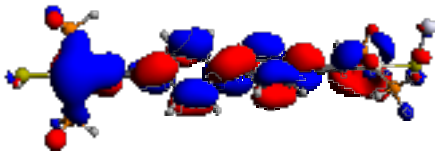


LUMO+2



LUMO+1



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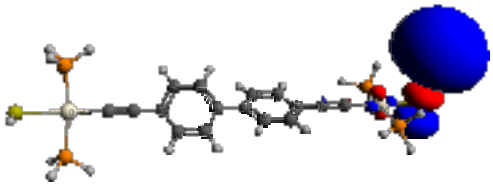
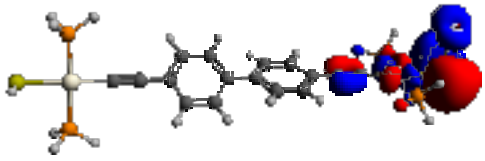


HOMO

HOMO-1



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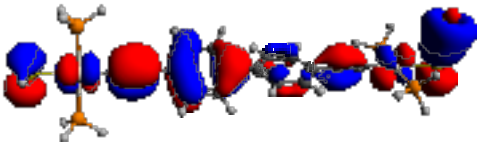
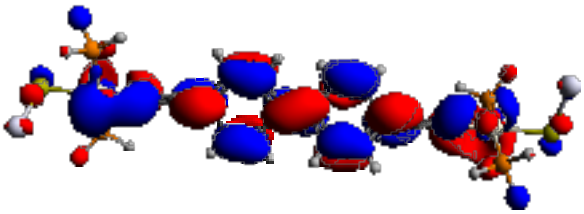


Ag-link-Ag

LUMO+2



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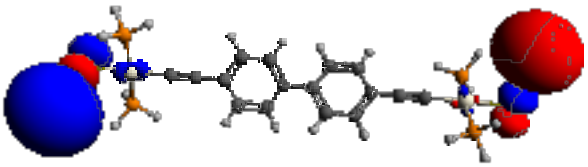

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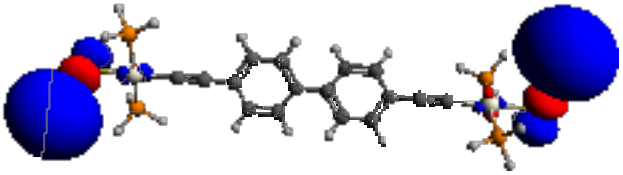

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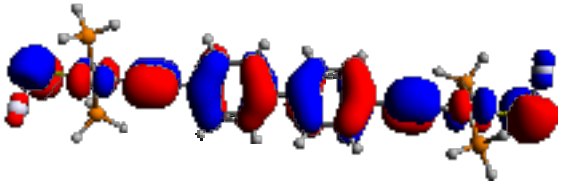

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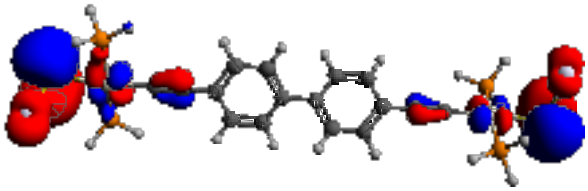

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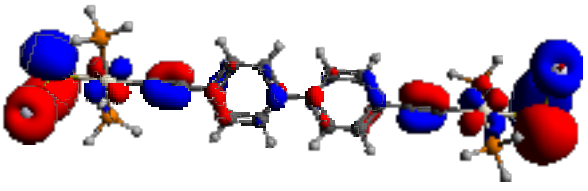

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